Since the 1990s, duplex stainless steels have been gaining ground over austenitics. Cost is only one factor: improved metallurgical techniques, improved weldability and greater availability of products have also played a role. Duplex alloys are now generally accepted as an efficient solution for corrosion issues in a number of process industries, while life-cycle cost and environmental factors are extending their use to other industries. This article outlines the history of the rise of duplex and enumerates the factors that will continue to make duplex an attractive material choice in the future.

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1. Metallurgical history of duplex grade

The history of duplex stainless steel has been extensively recounted in several studies [1–3]. Basing ourselves on these studies, we may outline the major steps as follows:

1.1 1930–1960

The first duplexes were mostly castings, since their improved resistance to hot cracking compared to austenitics made it easier to produce complicated shapes of castings. Pioneer companies such as Avesta, Creusot-Loire and Sandvik quickly invested to develop duplex grades, which were attractive because of their resistance to intergranular corrosion without requiring extremely low carbon contents (not easy to achieve at that time), and their higher mechanical properties compared to austenitics.

Nevertheless, high carbon contents could be detrimental in the predominantly ferritic heat-affected zones of welds, producing sensitization at the ferrite-ferrite grain boundaries (SCC risks).

Furthermore, the major difficulty was that the metallurgical variables to produce good duplex steels were not uniquely defined: as a consequence, these early-generation duplex steels were substantially one-company products, thus reducing availability and general acceptance.

1.2 1960–2000

As the refining techniques in electric arc furnaces were improved, it was possible to gradually lower carbon contents, to better control individual heat chemistries and to reduce impurity levels leading to major improvements in the quality of the delivered products. However, the major progress in the metallurgy of duplex stainless steel took place in the 1970s, with 4462/2205 emerging as the first generally accepted grade. It still accounts for over 70% of present duplex deliveries.

2. New developments in duplex stainless steel

Some new duplex grades have been introduced in the marketplace or are currently being developed in R&D departments. The main targets of such developments are determined by: (a) economy and overall cost benefits; (b) ease of fabrication: welding for plates or machining for bars; (c) improvements in design properties; (d) increased availability: stock and product forms; (e) increased know-how overcoming the fear of change.

2.1 Chemical analysis evolutions: new grade developments

The metallurgy evolution of the second generation (nitrogen-alloyed) duplex steels appears very clearly in a (Cr + Mo)% vs. N% diagram.

Nitrogen permits:
- control of the HAZ structure: since the introduction of the grade, there has been a growing tendency to increase levels of nitrogen from 0.1 to nearly 0.2%;
- reduction of the carbon contents to very low levels, thus helping to avoid problems related to ferrite-ferrite carbide precipitations;
- increase in the ferrite/austenite phase ratio to the more hot-workable 40-50% range.

All these factors explain the success of 2205, considered the prototype of duplex stainless steels to the point where “duplex steel” without further details now means 2205 duplex steel. The achievement of nitrogen levels at 0.2/0.27% permitted the development of super duplex grades such as S32750, S32520, S32760, with improved corrosion resistance (PREN ≥ 40).

Table 1. The most popular duplex grades in the 2000s.

<table>
<thead>
<tr>
<th>USA</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>N</th>
<th>Cu</th>
<th>Mn</th>
<th>Other</th>
<th>PREN</th>
</tr>
</thead>
<tbody>
<tr>
<td>S32304</td>
<td>1.4362</td>
<td>23</td>
<td>-</td>
<td>0.10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>24</td>
</tr>
<tr>
<td>S31803</td>
<td>1.4462</td>
<td>22</td>
<td>5.5/6</td>
<td>2.8/3.3</td>
<td>0.16/0.18</td>
<td>-</td>
<td>-</td>
<td>33</td>
</tr>
<tr>
<td>S32205</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>1/2</td>
<td>36</td>
</tr>
<tr>
<td>S32750</td>
<td>1.4410</td>
<td>25</td>
<td>7</td>
<td>3.5</td>
<td>0.25</td>
<td>-</td>
<td>1</td>
<td>41</td>
</tr>
<tr>
<td>S32520</td>
<td>1.4507</td>
<td>25</td>
<td>7</td>
<td>3.5</td>
<td>0.25</td>
<td>1/2</td>
<td>1</td>
<td>41</td>
</tr>
<tr>
<td>S32760</td>
<td>1.4501</td>
<td>25</td>
<td>7</td>
<td>3.5</td>
<td>0.22</td>
<td>0.6</td>
<td>W:0.6</td>
<td>40</td>
</tr>
</tbody>
</table>

New duplex grades developments have to take into account the following metallurgical stress considerations:
• Chromium + molybdenum contents below 21% are limited by the risk of martensite formation in the austenitic phase during cold deformation.
• Chromium + molybdenum contents over 35% are limited by the stability of the ferritic phase (precipitation of intermetallics).
• Earlier grades containing 0.1–0.2% nitrogen have now been replaced by higher-nitrogen versions. The addition of nitrogen is obviously limited by the nitrogen solubility limits (melting, welding).

Despite these limitations, numerous developments have been made which can be split into several categories.

2.2 Lean duplex
Nowadays the main target is the development of lean duplex, which have much fewer alloying elements than the standard 2205 duplex grade. Lean duplex has been replacing 316 and even 304 grades. The chemistries of some of these alloys are presented in Table 2.

Table 2. New lean duplex grades compared to 304L and 316L.

<table>
<thead>
<tr>
<th>USA</th>
<th>EN</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>N</th>
<th>Cu</th>
<th>Mn</th>
<th>Others</th>
<th>PREN</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>1.4307</td>
<td>18</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>1.4401</td>
<td>17</td>
<td>10–14</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>S32001</td>
<td>20</td>
<td>1.7</td>
<td>0.3</td>
<td>0.15</td>
<td>0.3</td>
<td>5</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S32101</td>
<td>1.4162</td>
<td>21.5</td>
<td>1.5</td>
<td>0.3</td>
<td>0.2</td>
<td>0.3</td>
<td>5</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>S32202</td>
<td>1.4062</td>
<td>22.7</td>
<td>2</td>
<td>0.3</td>
<td>0.21</td>
<td>0.2</td>
<td>1.3</td>
<td>26/27</td>
<td></td>
</tr>
<tr>
<td>S32003</td>
<td>20</td>
<td>3.5</td>
<td>1.7</td>
<td>0.15</td>
<td>-</td>
<td>2</td>
<td>28</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Indussteel produces 2202 and 2304 lean duplex grades, which offer excellent cost-effective alternatives to 304L and 316L in a number of applications.

2.3 Hyperduplex
In contrast (Fig. 2), attempts are being made to develop new hyperduplex grades, which present, in some applications, higher corrosion resistance than 6%Mo. Some of the respective chemistries are presented Table 3.

Table 3. Hyperduplex grades.

<table>
<thead>
<tr>
<th>USA</th>
<th>EN</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>N</th>
<th>Cu</th>
<th>Mn</th>
<th>Others</th>
<th>PREN</th>
</tr>
</thead>
<tbody>
<tr>
<td>S32906</td>
<td>29</td>
<td>6</td>
<td>2</td>
<td>0.4</td>
<td>0.5</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>42</td>
</tr>
<tr>
<td>S32707</td>
<td>27</td>
<td>7</td>
<td>5</td>
<td>0.4</td>
<td>0.3</td>
<td>1</td>
<td>0.76</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>S33207</td>
<td>30</td>
<td>8</td>
<td>4</td>
<td>0.5</td>
<td>0.1</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>51</td>
</tr>
</tbody>
</table>

The hyperduplex grades currently available have been largely used in the production of seamless tubes. They promise cost-effective alternatives to super-austenitics or nickel-based alloys for heat exchangers cooled by seawater.

2.4 Use of duplex at lower temperature
A better knowledge of duplex metallurgy has allowed us to obtain improved impact properties at low temperature. High purity, a well balanced analysis, an optimized thermomechanical cycle and lower ferrite content (30–50%) are factors allowing good impact strength at –80°C.

Indussteel is now able to guarantee 100J at –80°C (and 80J at –105°C) for “improved” duplex 2205.

2.5 Removing heat input requirements
Although no clear limits has ever been determined, it has always been considered safe to maintain a duplex structure in all parts of a weld. A safe rule would be to include more than 25% ferrite in the weld metal and less than 75% in the high-temperature heat affected zone. This rule has led to the definition of welding filler compositions on the one hand, and some minimum heat input restrictions on the other. These rules have been successfully applied in many applications but may prove difficult to apply in corner positions or welding processes without filler. However, we conclude that it is now possible to produce duplex material which will not be subject to the above-mentioned limitations.
2.6 Availability of products

(a) Flat products
Duplex stainless steels currently represent 10% of quarto-plate deliveries, but duplex CMP/coil products represent a smaller share of total stainless production. CR availability of duplex stainless steel is still limited, while CrMn (200 series) steels are increasing their market share for mildly corrosive applications. Nevertheless, strong investments and development programmes have recently been launched by major stainless steel coils producers in order to develop duplex coil production. This should certainly have an impact in the coming years on the products types share described in Fig. 6.

(b) Tubular products
The share of duplex is high for seamless tubes but lower in welded tubes.

c) Long products
The share of duplex in long products is growing.

![Fig. 6. Share of duplex steels per product form.](image)

3. Will duplex usage continue to grow?
Even though the market continues to be dominated by 304L and 316L, several factors are helping to bring about a greater variety of grades and tailor-made compositions (duplex, ferritics, etc.):

- impact of raw materials and volatility;
- calculations taking into account life cycle costing (LCC);
- international pressure for environmental preservation;
- competition between materials;
- growth in the newly industrialized areas, meaning a lower “barrier to change”.

3.1 Impact of raw materials and volatility
Due mainly to growth in the Asian economies and some difficulties in supply routes, raw materials prices (especially nickel and molybdenum, but more recently chromium also) climbed significantly, causing engineering companies and fabricators to switch away from austenitics (304, 316, 317LMN) and super austenitics to alternative grades. In addition to their interesting properties, the more stable price of duplex grades make them very attractive in the current market situation. Duplex alternatives are now challenging austenitics for each “level” of corrosion resistance depending on application:

- new lean duplex 2101 or 2202 as an alternative to 304;
- 2304 as an alternative to 316L;
- 2205 and super duplexes as alternatives to 317LMN or super austenitics.

![Fig. 7a and 7b. Impact of raw materials evolution on cost positioning: duplex and austenitics compared.](image)

3.2 Calculations taking into account life cycle costing
This second factor is a consequence of escalating maintenance costs in developed countries. LCC techniques are being more and more applied to evaluate material solution options in new investments and major revamping operations. Although LCC techniques are not fully established, they generally tend to demonstrate that the stainless option is generally more efficient after a few years than coated or painted carbon steel. Some important markets, such as pulp and paper, flue gas desulphurizing systems and fertilizers, moved to stainless steels and especially duplex grades many years ago. This renewed interest in LCC, especially maintenance costs, reinforces the interest of duplex stainless steels in new markets such as desalination. In the de-aerated part of MSF/MED processes 316L and 316Lmo has mainly been used, but now the trend is towards duplex 2304 or 2205.

![Fig. 8. Evolution of Industeel deliveries for desalination mill (about 23KT since 2000).](image)

For reverse osmosis processes, super duplex often competes with 6%Mo. Strength, availability and delivery times are, with relative prices obviously, the key factors in the material choice.
A more recent trend is the evaluation of the stainless steel option as a powerful tool to cut maintenance costs, not only in process systems but also in aesthetic applications such as welded structures and bridges.

These applications could revive stainless plate growth in mature markets and sectors with high labour and maintenance costs, where stagnant industrial investments limit the “natural” growth of the market.

In order to assist in this shift in material choice, Industeel has developed some specific LCC softwares:

- CALRES for storage tanks (calculation of initial and LCC of cylindrical vertical storage tanks built in different materials: coated CS, 304, 316, duplex, etc.);
- CALPIPE for water distribution pipes (comparing stainless piping and coated carbon steel);
- FGD systems comparing stainless and organics.

3.3 Environmental preservation

There is an increased pressure in many countries to reduce the impact on the environment of industrial and power generation activities. Many of the most effective measures have proved positive for stainless steel usage:

- reduced usage of paint and corrosion inhibitors in offshore operations;
- reduction of the acidity (SO₂, NOx) and opacity of flue gases in coal burning thermal power plants;
- reduction in CO₂ emissions, which favours hydropower, nuclear, etc.;
- much stricter purity standards in food, agriculture, water and health care products.

Duplex grades are now extensively used in scrubbers for FGD systems, thanks to:

- the visionary decisions of some pioneers: the first duplex scrubber was built at Gibson power station (USA) in the late 1980s (material: UNS S 32550);
- extensive corrosion studies by producers like Industeel and international organizations like the Nickel Institute, giving utilities and engineering firms very useful guides to choice.

4. Conclusion

The use of duplex grades has grown continuously since the 1990s. This growth has been accentuated by the current high cost of raw materials that makes duplex very cost-attractive compared to austenitics. Nevertheless, duplex development is also the consequence of several factors:

- progress in metallurgy, melting methods allowing chemical analysis optimization, hot workability and weldability improvements;
- improved availability in all shapes of products (plates, seamless and welded pipes, bars, coils);
- storage at distributors warehouses.

New grades will continue to be developed that will improve the properties of the duplex family:

- lean duplex competing with 304L or 316L;
- hyperduplex competing with 6%Mo;
- chemical analysis optimization allowing use down to −100°C and lightening of welding parameters requirements.

Resistance to change is important in varying degrees depending on markets: nevertheless, duplex is accepted as an efficient solution to corrosion issues in pulp and paper, chemical carriers, oil and gas, FGD systems, etc. New key factors such as LCC calculations and international pressure for environmental preservation are causing a shift to duplex use in other applications (desalination, architecture, storage tanks), ensuring without any doubt further development for the whole duplex family.

References


ABOUT JEAN-CHRISTOPHE GAGNEPAIN

Jean-Christophe Gagnepain graduated as a materials engineer from the INSA at Lyon, France. He joined the Industeel Research Center in 1990 as the Manager of the Metallurgy Department for Corrosion Resistant Alloys dedicated to new products and process developments and the provision of technical expertise to customers. In 1997 he moved to Industeel’s plate mill, where he spent six years as the Manager of the Methods/Quality Department for the whole range of Industeel products. From 2003 he has worked as their Sales Manager for Stainless Steels and Clad Plates and is currently Marketing Manager for Stainless Steels and Clad Plates.